

PATENT SPECIFICATION

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- (21) Application No. 16945/77 (22) Filed 22 April 1977
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(54) DETERGENT COMPOSITIONS

(71) We, PROCTER & GAMBLE LIMITED, a company organised under the laws of the United Kingdom, of Hedley House, Gosforth, Newcastle Upon Tyne, NE99 1EE, England, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to detergent compositions for washing and laundering fabrics. In particular, it relates to detergent compositions incorporating phosphorus-containing detergency builders and which additionally incorporate a multi-component builder auxiliary system comprising a specified mixture of polyacid sequestering agents for improving the cleaning and whiteness maintenance performance of the composition while reducing its washing machine scaling and fabric ash deposition characteristics.

The problems of whiteness loss and ash deposition are particularly pronounced when fabrics are washed with a detergent composition containing a significant amount of water-soluble orthophosphate and/or water-soluble pyrophosphate. These are known to occur as degradation products of sodium tripolyphosphate when a detergent composition containing it is prepared by spray-drying. The degree of degradation is generally greater than 10% by weight of the phosphate builder, is commonly from 15 to 30% of the builder and can, on occasion, reach 40% by weight of the builder. In addition aqueous detergent compositions built with tripolyphosphate also contain some ortho and/or pyrophosphate by hydrolytic degradation of the tripolyphosphate in the liquid medium. For these reasons, therefore, the whiteness maintenance and ash deposition performance of conventionally formulated tripolyphosphate built detergents can suffer markedly as a result of degradation in manufacture, storage or use, and these performance negatives are found to be particularly pronounced when the products are either used in an "under-built" manner (i.e. a ratio of builder to hardness ions of less than 1:1) or when they are actually formulated with lower than conventional levels of tripolyphosphate builder.

Ortho and pyrophosphates are, of course, useful builders in their own right, and have come into more prominence in recent years as the use of high levels of sodium tripolyphosphate has come under scrutiny because of the suspicion that soluble phosphate species accelerate the eutrophication or aging process of water bodies. This eutrophication is ordinarily evidenced by the rapid growth of algae in the water body. As more fully explained in German Offenlegungsschrift No. 21605,052 ortho- and pyrophosphates, specially orthophosphate, can remove more hardness ions (Ca^{++} , Mg^{++}) per unit of P_2O_5 in their constitution than can tripolyphosphate. Orthophosphates, and to a greater or less extent, pyrophosphates, act as detergency builders however, by precipitating these hardness ions as insoluble phosphates wherein sodium tripolyphosphate retains them in solution as complex ions. Building detergency by means of this precipitating mechanism tends, therefore, to cause undesirable effects.

In particular, the precipitation of these phosphate salts can take place on the fabrics being cleaned or upon the surfaces of the washing machine. Such buildup of insoluble phosphate is undesirable in that the precipitates have a tendency to remain on the fabrics through several washing cycles and continue to build up, thus causing greyness and harshness of feel. Similarly, the calcium phosphate may, after

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several cycles in a washing machine, cause unsightly and undesirable deposition or scale on exposed surfaces of washing machine drums and, especially, heating elements. This precipitation phenomenon of ortho and pyrophosphate has led many detergent manufacturers to avoid these materials and instead to use tripolyphosphates.

Another consideration in formulating phosphate-built detergents is the effect of transition metal ions and ion complexes on cleaning performance. Transition metals are common trace impurities in detergent wash liquors, being introduced, for instance, in the wash solution feed liquor, or in the fabric soil or as impurities in the detergent composition raw materials such as alkali metal silicates. Even at trace levels, transition metal ions and complexes can detrimentally effect cleaning performance, for instance, by intensifying or modifying the hue of stains and soils on fabrics or, more indirectly, by catalysing the degradation or peroxygen bleach. Although a combination of phosphate and a conventional polyacid sequestering agent such as tetrasodium ethylenediamine tetraacetate is found to be readily effective in controlling transition metals present in solution in the form of simple ions, control of transition metals in the form of complex ions or bound to fabric surfaces has proved, on the other hand, to be a far more intractable problem which is not amenable to solution by conventional means.

Another aspect of the cleaning problem in phosphate-built detergent compositions concerns the role played by auxiliary enzyme and persalt bleaching agents. It is well known that the overall cleaning performance of phosphate built compositions containing enzymes and persalt bleaching agents is limited by the fact that the commercially available enzymes have optimum cleaning effectiveness at relatively low solution pH (usually pH 9 to 9.5) and low wash temperature (e.g. up to 60°C), while the common persalt bleaching agents have optimum effectiveness at high solution pH and high wash temperature. As a result it is difficult to secure good cleaning performance at all wash temperatures on both proteinaceous and bleachable soils and stains, without adopting excessively complicated washing practices.

All of the components of the builder and builder auxiliary system of the composition of the present invention have, individually, been proposed for various purposes in fabric washing compositions. Thus British Patent 1,021,017 discloses built detergent compositions having improved whiteness maintenance, containing lower poly phosphate salts and ethane-1-hydroxy-1,1-diphosphonic acid. British Patent 1,424,356 also discloses the use of low levels of ethane-1-hydroxy-1,1-diphosphonic acid in phosphate-built detergents in order to improve whiteness maintenance. Belgium Patent 738,670 describes the use of ethylenediamine tetra(methylene phosphonates) for improving the whiteness maintenance of phosphate built detergents. British Patent 1,226,314 discloses the use of mixtures of aminoalkylenephosphonic acids and polyacrylic acids for use in alkaline cleaning compositions. British Patent 1,398,263 describes the addition of various polyacid anti-deposition agents in carbonate build compositions.

Despite the substantial amount of prior art describing the use of polyacids and salts as builder and detergent composition ingredients, it has not apparently been hitherto recognised that a minor amount of a combination of selected polyacids can significantly improve the performance of detergent formulations built with ortho, pyro and/or tripolyphosphate builders at both conventional and low phosphate levels, in the areas in which such formulations are deficient, namely the areas of whiteness maintenance, ash deposition, washing machine deposition and cleaning performance on clay, proteinaceous and oxidizable soils.

According to the present invention, there is provided a built detergent composition having a pH in 0.5% aqueous solution of less than 11.5%, the composition comprising:

- (a) from 1 to 90% of an organic detergent selected from anionic, nonionic, amphoteric, and zwitterionic detergents and mixtures thereof,
- (b) from 1 to 70% of a phosphate builder selected from orthophosphate, pyrophosphate and tripolyphosphate salts, and mixtures thereof, and
- (c) at least 0.2% of a builder auxiliary comprising a mixture of:
 - (i) up to 4% by weight of a polyphosphonic acid or salt thereof, and
 - (ii) up to 4% by weight of a homo- or co-polymeric polycarboxylic acid or salt thereof, said polycarboxylic acid having a formula comprising at least two carboxyl radicals separated from each other by not more than two carbon atoms.

The detergent compositions of the invention contain as essential ingredients a synthetic organic detergent, a phosphate builder salt, and a builder auxiliary comprising a polyacid mixture. The detergent composition has a solution pH, defined as the pH of a 0.5% aqueous solution of the composition of less than 11.5. In preferred compositions, the solution pH is less than 10.5, more preferably less than 10.0, these pH constraints being found to optimize the detergency characteristics of the composition of the invention.

The essential and optional components of these compositions will now be described in detail.

Organic Detergent

The detergent component of the present compositions can be anionic, nonionic, ampholytic, or zwitterionic in nature, or can be mixtures thereof. The organic detergent constitutes from 1 to 90%, especially from 3 to 75% by weight of the composition, but for solid granular compositions the content of organic detergent is generally in the range from 5 to 40%, more preferably, from 10 to 30% by weight of the compositions. In liquid detergent compositions, the content of organic detergent can be as high as from 20 to 70% by weight.

A typical listing of anionic, nonionic, zwitterionic and amphoteric surfactants useful herein appears in U.S.P. 3,925,678 incorporated herein by reference. The following list of detergent compounds which can be used in the instant compositions is representative of such materials.

Water-soluble salts of the higher fatty acids, i.e. "soaps", are useful as the anionic detergent component of the compositions herein. This class of detergents includes ordinary alkali metal soaps such as the sodium, potassium, ammonium and alkylammonium salts of higher fatty acids containing from 8 to 24 carbon atoms and preferably from 10 to 20 carbon atoms. Soaps can be made by direct saponification of fats and oils or by the neutralization of free fatty acids. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e. sodium or potassium tallow and coconut soap.

A highly preferred class of anionic detergents includes water-soluble salts, particularly the alkali metal, ammonium and alkylammonium salts, of organic sulfuric reaction products having in their molecular structure an alkyl group containing from 8 to 22, especially from 10 to 20 carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of acyl groups). Examples of the detergent compositions of the present invention are the sodium and potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols C_8-C_{18} carbon atoms) produced by reducing the glycerides of tallow or coconut oil; and sodium and potassium alkyl benzene sulfonates, in which the alkyl group contains from 9 to 15 carbon atoms, in straight chain or branched chain configuration, e.g. those of the type described in U.S.P. 2,220,099 and 2,477,383. Especially valuable are linear straight chain alkyl benzene sulfonates in which the average of the alkyl group is about 11.8 carbon atoms, abbreviated as $C_{11.8}$ LAS.

A preferred alkyl ether sulfate surfactant component of the present invention is a mixture of alkyl ether sulfates, said mixture having an average (arithmetic mean) carbon chain length within the range of 12 to 16 carbon atoms, preferably from 14 to 15 carbon atoms, and an average (arithmetic mean) degree of ethoxylation of from 1 to 4 mols of ethylene oxide.

Other anionic detergent compounds herein include the sodium alkyl glyceryl ether sulfates, especially those ethers of higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfonates and sulfates; and sodium or potassium salts of alkyl phenol ethylene oxide ether sulfate containing 1 to 10 units of ethylene oxide per molecule and wherein the alkyl groups contain 8 to 12 carbon atoms.

Other useful anionic detergent compounds herein include the water-soluble salts of esters of α -sulfonated fatty acids containing from 6 to 20 carbon atoms in the fatty acid group and from 1 to 10 carbon atoms in the ester group; water-soluble salts of 2-acyloxy-alkane-1-sulfonic acids containing from 2 to 9 carbon atoms in the acyl group and from 9 to 23 carbon atoms in the alkane moiety; alkyl ether sulfates containing from 10 to 20 carbon atoms in the alkyl group and from 1 to 30 moles of ethylene oxide; water-soluble salts of olefin sulfonates containing from 12 to 24 carbon atoms; water-soluble salts of paraffin sulfonates containing from 8 to 24, especially 14 to 18 carbon atoms, and β -alkoxy alkane sulfonates containing

from 1 to 3 carbon atom in the alkyl group and from 8 to 20 carbon atoms in the alkane moiety.

Anionic surfactant mixtures can also be employed, for example 5:1 to 1:5 mixtures of an alkyl benzene sulfonate having from 9 to 15 carbon atoms in the alkyl radical and mixtures thereof, the cation being an alkali metal preferably sodium; and from 2% to 15% by weight of an alkyl ethoxy sulfate having from 10 to 20 carbon atoms in the alkyl radical and from 1 to 30 ethoxy groups and mixtures thereof, having an alkali metal cation, preferably sodium.

Water-soluble nonionic synthetic detergents are also useful as the detergent component of the instant composition. Such nonionic detergent materials can be broadly defined as compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. The length of the polyoxyalkylene group which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

Examples of suitable nonionic detergents include:

1. The polyethylene oxide condensates of alkyl phenol, eg. the condensation products of alkyl phenols having an alkyl group containing from 6 to 12 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to 5 to 25 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds may be derived, for example, from polymerised propylene, di-isobutylene, octene or nonene. Other examples include dodecylphenol condensed with 12 moles of ethylene oxide per mole of phenol; dinonylphenol condensed with 15 moles of ethylene oxide per mole of phenol; nonylphenol condensed with 20 moles of ethylene oxide per mole of nonylphenol and di-iso-octylphenol condensed with 15 moles of ethylene oxide.

2. The condensation product of primary or secondary aliphatic alcohols having from 8 to 24 carbon atoms, in either straight chain or branched chain configuration, with from 1 to 30 moles of alkylene oxide per mole of alcohol. Preferably, the aliphatic alcohol comprises between 9 and 15 carbon atoms and is ethoxylated with between 2 and 12, desirably between 3 and 8 moles of ethylene oxide per mole of aliphatic alcohol. Such nonionic surfactants are preferred from the point of view of providing good to excellent detergency performance on fatty and greasy soils, and in the presence of hardness sensitive anionic surfactants such as alkyl benzene sulphonates. The preferred surfactants are prepared from primary alcohols which are either linear (such as those derived from natural fats or prepared by the Ziegler process from ethylene, eg. myristyl, cetyl, stearyl alcohols), or partly branched such as the Dobanols and Neodols which have about 25% 2-methyl branching (Dobanol and Neodol being Trade Names of Shell) or Synperionics, which are understood to have about 50% 2-methyl branching (Synperionic is a trade name of I.C.I.) or the primary alcohols having more than 50% branched chain structure sold under the Trade Name Lial by Liquichimica. Specific examples of nonionic surfactants falling within the scope of the invention include Dobanol 45-4, Dobanol 45-7, Dobanol 45-11, Dobanol 91-3, Dobanol 91-6, Dobanol 91-8, Synperonic 6, Synperonic 14, the condensation products of coconut alcohol with an average of between 5 and 12 moles of ethylene oxide per mole of alcohol, the coconut alkyl portion having from 10 to 14 carbon atoms, and the condensation products of tallow alcohol with an average of between 7 and 12 moles of ethylene oxide per mole of alcohol, the tallow portion comprising essentially between 16 and 22 carbon atoms. Secondary linear alkyl ethoxylates are also suitable in the present compositions, especially those ethoxylates of the Tergitol series having from 9 to 16 carbon atoms in the alkyl group and up to 11, especially from 3 to 9, ethoxy residues per molecule.

3. The compounds formed by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The molecular weight of the hydrophobic portion generally falls in the range of 1500 to 1800. Such synthetic nonionic detergents are available on the market under the trade name of "Pluronic" supplied by Wyandotte Chemicals Corporation.

Semi-polar nonionic detergents include water-soluble amine oxides containing one alkyl moiety of from 10 to 28 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from 1 to 3 carbon atoms; water-soluble phosphine oxide detergents containing one alkyl moiety of 10 to 23 carbon atoms and 2 moieties selected from the group consisting

of alkyl groups and hydroxyalkyl groups containing from 1 to 3 carbon atoms; and water soluble sulfoxide detergents containing one alkyl moiety of from 10 to 28 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from 1 to 3 carbon atoms.

5 Ampholytic detergents include derivatives of aliphatic or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic moiety can be straight chain or branched and wherein one of the aliphatic substituents contains from 8 to 18 carbon atoms and at least one aliphatic substituent contains an anionic water-solubilizing group. 5

10 Zwitterionic detergents include derivatives of aliphatic quaternary ammonium, phosphonium and sulfonium compounds in which the aliphatic moieties can be straight chain or branched, and wherein one of the aliphatic substituents contains from 8 to 18 carbon atoms and one contains an anionic water-solubilizing group. Further use of zwitterionic detergents are discussed in U.S. Patents Nos. 3,925,262 and 3,929,678. 10

15 It is to be recognised that any of the foregoing detergents can be used separately herein or as mixtures. 15

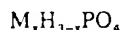
A highly preferred mixture of surfactants is an anionic/nonionic mixture, especially a mixture of a C_8 — C_{22} alkyl benzene sulfonate and a C_{10} — C_{20} alkanol ethoxylated with from 3 to 30 moles of ethylene oxide per mole of alkanol. Highly preferred mixtures include C_{12} alkyl benzene sulfonate and C_{14} — C_{18} alcohol-(7)-ethoxylate, in ratios of from 5:1 to 1:3, preferably 3:1 to 1:1. In still more preferred compositions, a fatty acid soap is added to the above-described mixture, preferably a C_{10} — C_{20} soap at a level of from 1% to 5%. 20

25 Builder 25

The essential builder component is selected from orthophosphate, pyrophosphate and tripolyphosphate salts, in particular, the alkali metal, ammonium and substituted ammonium salts. These are present in the finished product at a level of from 1 to 70% by weight of the composition, preferably from 5 to 50%. The low phosphate compositions of the invention contain from 6 to 30%, preferably from 10 to 25% of phosphate builder salt. Expressed in terms of overall phosphorus content, the compositions of the invention generally contain phosphorus in an amount less than that contained in a 45% sodium tripolyphosphate built composition. In low phosphate compositions, however, there is preferably no more phosphorus than that equivalent to 30%, more preferably 20% of sodium tripolyphosphate. The preferred builder component in the compositions of the invention is penta sodium tripolyphosphate, although it will be appreciated that conventional spray-drying of tripolyphosphate built detergents can lead to partial degradation of the builder with consequent formation of low levels of ortho- and pyrophosphate salts. Thus, the compositions of the invention will in general contain at least 2%, especially at least 4% by weight of the builder of orthophosphate salts, and/or at least 7%, especially at least 10% of the builder of pyrophosphate salts. 30

Ortho- and pyrophosphate salts can also be separately added to the compositions of the invention, however, either in addition to or replacing the tripolyphosphate builder. 35

45 Suitable orthophosphate salts can be represented by the general formula 45



wherein M is an alkali metal, ammonium or substituted ammonium cation, and x is 1, 2 or 3. Preferably M is sodium or potassium, especially sodium, although liquid detergent compositions of the invention can contain builder in the form of the ammonium or alkanolammonium salts, e.g., the salts formed from monoethanolamine, diethanolamine, triethanolamine and mixtures thereof. Normally, alkali metal salts are present in granular detergents in the form of crystalline hydrates having up to 12 moles of water associated with each mole of alkali metal phosphate. Ammonium and substituted ammonium salts can be obtained commercially or can be formed by neutralization of orthophosphoric acid or acid salt. 50

Generally, orthophosphate is added to the compositions of the invention at a level in the range from 1 to 50%, preferably from 2 to 30% by weight. One preferred class of compositions comprises orthophosphate at a level of at least 40% by weight of the total phosphorus-containing builder salt. These compositions preferably 60

contain from 6 to 25%, especially from 7 to 20%, and more especially from 8 to 18% by weight of orthophosphate salt.

Pyrophosphate is an additional optional but preferred component of the compositions of the present invention. Readily available commercially are tetrasodium pyrophosphate $\text{Na}_4\text{P}_2\text{O}_7$, and its decahydrate $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$, 5 tetrapotassium pyrophosphate $\text{K}_4\text{P}_2\text{O}_7$, sodium acid pyrophosphate or "acid pyro" $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$, and its hexahydrate $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7 \cdot 6\text{H}_2\text{O}$, and pyrophosphoric acid $\text{H}_4\text{P}_2\text{O}_7$. Monosodium pyrophosphate and trisodium pyrophosphate also exist, the latter as the anhydrous form or the mono- or nona-hydrate. The generic formula 10 for the anhydrous forms of these compounds can be expressed as $\text{M}_x\text{H}_y\text{P}_2\text{O}_7$, where M is alkali metal and x and y are integers having the sum of 4.

Generally, pyrophosphate is added to the compositions of the invention at a level in the range from 1 to 60%, preferably from 2 to 35% by weight. One preferred class of compositions comprises pyrophosphate and tripolyphosphate salts at a weight ratio lying in the range from 5:1 to 1:4, especially from 3:1 to 1:1. In such 15 compositions, the orthophosphate content is preferably kept to a minimum and in particular the weight ratio of pyrophosphate to orthophosphate salts should be greater than 7:1. Low phosphate compositions based on this builder system preferably comprise up to 25% and more preferably from 10 to 20% by weight of the builder system; up to 20% and more preferably from 5 to 16% by weight of the 20 pyrophosphate salt; and up to about 15%, more preferably from 4 to 8% of the tripolyphosphate salt.

When the builder system is based upon mixtures of ortho and pyrophosphate salts it is desirable that the weight ratio of orthophosphate to pyrophosphate salts is 25 in the range from 10:1 to 1:10, preferably from 9:1 to 3:7, more preferably from 8:2 to 4:6 and even more preferably from 3:1 to 1:1.

One class of the compositions containing both ortho and pyrophosphate salts suitable for use in the present invention has a weight ratio of orthophosphate to pyrophosphate salts lying in the range from 65:35 to 50:50 and has a weight ratio of tripolyphosphate salt to the sum total of ortho and pyrophosphate salts of less than 1:1. In another class of compositions containing both orthophosphate and 30 pyrophosphate salts, the weight ratio of tripolyphosphate salt to the sum total of ortho and pyrophosphate salt lies in the range from 1:1 to 9:1, especially from 1.05:1 to 3:1 and more especially from 1.1:1 to 1.5:1. In this class of composition, the ratio of orthophosphate to pyrophosphate salts preferably lies in the range from 5:2 to 35 3:2, and the composition preferably contains no more phosphorus than that contained in 20% tripolyphosphate.

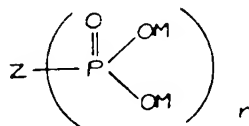
Builder Auxiliary

A further essential integer of the invention is a builder auxiliary comprising a 40 mixture of

- (i) up to 4% by weight of a polyphosphonic acid or salt thereof,
- (ii) up to 4% by weight of a homo- or copolymeric polycarboxylic acid or salt thereof, said polymeric acid comprising monomer units of a 45 polycarboxylic acid having at least two carboxyl radicals separated from each other by not more than two carbon atoms.

The builder auxiliary is desirably present at a level of at least 0.2% by weight of the composition, preferably from 0.4 to 5% and especially from 1.0 to 3% by weight of the composition. The ratio of builder to builder auxiliary generally lies in the range from 100:1 to 3:1, especially from 30:1 to 5:1. The level of the 50 polyphosphonate and polymeric polycarboxylate components can separately lie in the range from 0.1 to 4%, preferably from 0.5 to 3.5% by weight of the composition.

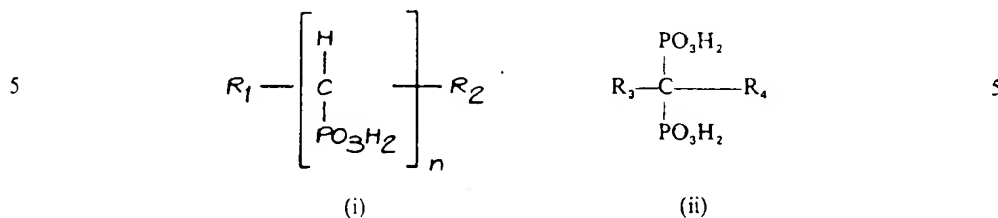
Preferred polyphosphonates are those of the general formula



wherein n is at least 2, M is an alkali metal, ammonium or substituted ammonium cation and Z is a connecting organic moiety having an effective covalency equal to n. Preferably Z is a hydrocarbyl or hydrocarbyl substituted amino radical. Various 55

specific classes of polyphosphonates useful in the present invention, are indicated below.

The polyphosphonate can be derived from acids selected from the group consisting of those of the formulae:



wherein R_1 and R_2 are hydrogen or CH_2OH ; n is an integer of from 3 to 10; R_3 is hydrogen, alkyl containing from 1 to 20 carbon atoms, alkenyl containing from 2 to 20 carbon atoms, aryl (e.g., phenyl and naphthyl), phenylethenyl, benzyl, halogen (e.g., chlorine, bromine, and fluorine), amino, substituted amino (e.g., dimethylamino, diethylamino, N-hydroxy-N-ethylamino, acetylamino), $-CH_2COOH$, $-CH_2PO_3H_2$, $-CH(PO_3H_2)(OH)$ or $-CH_2CH(PO_3H_2)_2$; and R_4 is hydrogen, lower alkyl (e.g., chlorine, bromine and fluorine), hydroxyl, $-CH_2COOH$, $-CH_2PO_3H_2$, or $-CH_2CH_2PO_3H_2$.

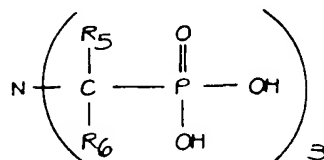
Operable polyphosphonates of the above formula (i) include propane - 1,2,3 - triphosphonic acid; butane - 1,2,3,4 - tetraphosphonic acid; hexane - 1,2,3,4,5,6 - hexaphosphonic acid; hexane - 1 - hydroxy - 2,3,4,5,6 - pentaphosphonic acid; hexane - 1,6 - dihydroxy - 2,3,4,5 - tetraphosphonic acid; pentane - 1,2,3,4,5 - pentaphosphonic acid; heptane - 1,2,3,4,5,6,7 - heptaphosphonic acid; octane - 1,2,3,4,5,6,7,8 - octaphosphonic acid; nonane - 1,2,3,4,5,6,7,8,9 - nonaphosphonic acid; decane - 1,2,3,4,5,6,7,8,9,10 - decaphosphonic acid; and the salts of these acids, e.g., sodium, calcium, magnesium, ammonium, triethanolammonium, diethanolammonium, and monoethanolammonium salts.

Among the operable polyphosphates encompassed by the above formula (ii) are ethane - 1 - hydroxy - 1,1 - diphosphonic acid; methanediphosphonic acid; methanedi-hydroxydiphosphonic acid; ethane - 1,1,2 - triphosphonic acid; propane - 1,1,3,3 - tetraphosphonic acid; ethane - 2 - phenyl - 1,1 - diphosphonic acid; ethane - 2 - naphthyl - 1,1 - diphosphonic acid; methanephenyldiphosphonic acid; ethane - 1 - amino - 1,1 - diphosphonic acid; methanedichlorodiphosphonic acid; nonane - 5,5 - diphosphonic acid; n - pentane - 1,1 - diphosphonic acid; methanedifluorodiphosphonic acid; methanedibromodiphosphonic acid; propane - 2,2 - diphosphonic acid; ethane - 2 - carboxy - 1,1 - diphosphonic acid; propane - 1 - hydroxy - 1,1,3 - triphosphonic acid; ethane - 2 - hydroxy - 1,1,2 - triphosphonic acid; ethane - 1 - hydroxy - 1,1,2 - triphosphonic acid; propane - 1,3 - diphenyl - 2,2 - diphosphonic acid; nonane - 1,1 - diphosphonic acid; hexadecane - 1,1 - diphosphonic acid; pent - 4 - ene - 1 - hydroxy - 1,1 - diphosphonic acid; octadec - 9 - ene - 1 - hydroxy - 1,1 - diphosphonic acid; 3 - phenyl - 1,1 - diphosphonoprop - 2 - ene; octane - 1,1 - diphosphonic acid; dodecane - 1,1 - diphosphonic acid; phenylaminomethanediphosphonic acid; naphthylaminomethane - diphosphonic acid; N,N - dimethylaminomethanediphosphonic acid; N - (2 - hydroxyethyl) - aminomethanediphosphonic acid; N - acetylaminomethanediphosphonic acid; aminomethanediphosphonic acid; and the salts of these acids, e.g., sodium, potassium, calcium, magnesium, ammonium, triethanolammonium, diethanolammonium and monoethanolammonium salts.

Mixtures of any of the foregoing phosphonic acids and/or salts can be used in the compositions of this invention. Methods of preparing these classes of materials are described in U.S. Patent No. 3,488,419.

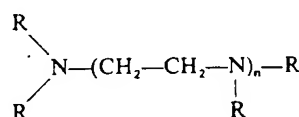
For the purpose of this invention, it is preferred that the polyphosphonates are free of hydroxyl groups.

Another useful and preferred class of polyphosphonates are the aminotrialkylidene phosphonates; these include acids of the general formula



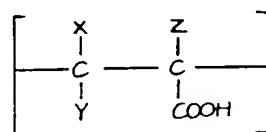
wherein R_5 and R_6 represent hydrogen or C_1 — C_4 alkyl radicals. Examples of compounds within this general class are aminotri(methylenephosphonic acid), aminotri(ethylidenephosphonic acid), aminotri(isopropylidenephosphonic acid), aminodi(methylenephosphonic acid)-mono(ethylidenephosphonic acid) and aminomono(methylenephosphonic acid) di(isopropylidenephosphonic acid).

Another useful and highly preferred class of polyphosphonates are the amino poly (alkylene phosphonates), particularly those having the general formula



wherein n is an integral number from 1 to 14, and each R is individually hydrogen or $\text{CH}_2\text{PO}_3\text{H}_2$ or a water-soluble salt thereof, provided that at least half of the radicals represented by R are $\text{CH}_2\text{PO}_3\text{H}_2$ radicals or water-soluble salts thereof. Especially preferred are diethylenetriamine penta (methylene phosphonic acid) and, more especially ethylene diamine tetra (methylene phosphonic acid).

With regard to the polymeric polycarboxylates, these preferably comprise polycarboxylic acid units or salts thereof having the general formula

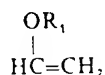


wherein X , Y , and Z are each selected from the group consisting of hydrogen, methyl, aryl, alkaryl, carboxyl, hydroxyl and carboxymethyl; at least one of X , Y , and Z being selected from the group consisting of carboxyl and carboxymethyl, provided that X and Y can be carboxymethyl only when Z is selected from carboxyl and carboxymethyl and wherein only one of X , Y , and Z can be methyl, aryl, hydroxyl and alkaryl.

Suitable polycarboxylates include those derived from maleic acid, citraconic acid, aconitic acid, fumaric acid, mesaconic acid, phenyl maleic acid, benzyl maleic acid, itaconic acid and methylene malonic acid monomers, or from the anhydrides of the above monomers where these exist.

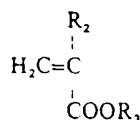
Preferably the polycarboxyl monomers provides at least about 33 and more preferably at least 45 mole percent of the monomeric species comprising the polymer species. The polymer can be selected from homopolymers of the above polycarboxyl monomers; or copolymers of two or more of the above polycarboxyl monomers; or copolymers of one or more of the above polycarboxyl monomers with an unsaturated polymerisable monomer other than the specified polycarboxyl monomers.

In general terms, suitable polymerizable unsaturated monomers include (a)



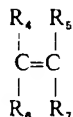
wherein R_1 is a C_1 to C_{12} alkyl group or a C_1 to C_{12} acyl group, R , optionally being hydroxy substituted,

(b)



wherein R_2 is H or CH_3 and R_3 is H, or a C_1 to C_{10} alkyl group, R_2 , R_3 optionally being hydroxy substituted,

(c)



wherein each of R_4 to R_7 is H or an alkyl group such that R_4 to R_7 , together have from 1 to 20 carbon atoms, R_4 — R_7 , each optionally being hydroxy substituted,

(d) N-vinyl pyrrolidone,

(e) Styrene.

Highly preferred polymeric polycarboxylates in the present invention are the copolymers of maleic acid with the above unsaturated monomers, optionally wholly or partly neutralised by sodium or potassium. All may be made by heating together maleic anhydride and the other monomer in an appropriate solvent, such as benzene, cyclohexene, or in some cases in excess of one of the monomers, in the presence of a catalyst such as an organic peroxide or azo-bisbutyronitrile. As will be appreciated by those skilled in the art, different solvents, catalysts, and reaction conditions are most suitable according to the type of copolymer and molecular weight thereof being prepared. In particular in order to make the high molecular weight polymers for the present invention, it is often desirable to use up the initiator (catalyst) to make a macro-radical and then to add further monomers employing the macro-radical as sole initiator. Methods of preparing these compounds are described in U.S. Patent No. 2,430,313 (Vana to E. I. Dupont de Nemours Co.). The polymers so prepared are, of course, copolymers of maleic anhydride and the selected monomer. Either before or during the manufacture of the compositions of the invention, these are usually hydrolysed to the acid form and optionally neutralised as indicated above.

In the present specification, unless stated otherwise, the molecular weight of the polymeric polycarboxylate is expressed as that of the unneutralised acid form thereof. Generally, the average molecular weight falls in the range from 500 to 2,000,000.

The alkyl vinyl ethers of class (a) above are preferably methyl vinyl ethers. Preferred molecular weights for these copolymers are in the range from 12,000 to 1,500,000, more preferably 50,000 to 300,000. Copolymers in anhydride form believed to be of this class are commercially available from GAF Corporation under the trade names Gantrez AN119 (MWt. 200,000 in anhydride form), Gantrez AN139 (MWt. 500,000 in anhydride form), AN149 (MWt. 750,000 in anhydride form) and AN169 (MWt. 1,125,000 in anhydride form). Ethyl and methyl vinyl ether/maleic anhydride copolymers are also available from BASF under the trade name Sokalan and having molecular weight about 30,000.

The molecular weight of these copolymers is the viscosity average molecular weight and is determined as follows:

A number of polymer solutions of known concentration (<1% w/v) are made up in a suitable solvent and their viscosities determined as described in F. Daniels *et al.*, Experimental Physical Chemistry, pp. 71—74, 242—246, McGraw-Hill (1949), at 25°C. using an Ostwald viscometer. A plot of (specific viscosity/concentration) against concentration is then constructed and the best line extrapolated to zero concentration. The value of (specific viscosity/concentration) at zero concentration is termed the intrinsic viscosity, $[\eta]$. This parameter is used to determine a viscosity-average molecular weight, M_v .

For the above copolymers as anhydrides the equation applicable employing acetone as solvent, and giving the molecular weight of the anhydride form, is:

$$\log[\eta]=0.94 \log \bar{M}_n-3.27 \quad \text{I}$$

In 1M NaOH, giving the molecular weight of the sodium salt of the copolymer, the equation is:

$$\log[\eta]=0.86 \log \bar{M}_n-2.88 \quad \text{II}$$

The acrylic-maleic copolymer derived from monomers of class (b) above are preferably based upon methyl acrylate or methyl methacrylate, although higher alkyl esters can be employed. The manufacture of these polymers, and the control of the molar ratio of the monomers one to other is described by Seymour, Harris and Branum in Industrial and Engineering Chemistry, Volume 41, pages 1509 to 1513, 1949. Preferably copolymers wherein the molar ratio of acrylate ester to maleic acid is from 2:1 to 1:1 are employed herein, especially close to 1:1; their molecular weight is preferably in the range from 3,000 to 1,500,000, especially from 5,000 to 30,000.

The molecular weight of these copolymers is determined by the method described above.

When an olefin of class (c) is used, the copolymers are preferably of high molecular weight and are preferably based on ethylene. The preferred molecular weight range is from 275,000 to 1,500,000.

Another preferred group of materials within this class are copolymers of maleic anhydride or acid with propylene, isobutylene, alkyl substituted isobutylene and, especially, di-isobutylene, having molecular weight in the range from 500 to 50,000 and molar ratio of olefine to maleic acid in the range from 1:1 to 1:2. Suitable materials of this type are available under the trade names "Empicryl" of Albright and Wilson Limited, and "Orotan" of Rohm and Haas.

The molecular weight of these polymers is determined by the method described above but employing ethanol as solvent and using the equation:

$$\log[\eta]=1.18 \log \bar{M}_n-3.85 \quad \text{III}$$

The vinyl pyrrolidone maleic copolymers preferably have molecular weights in the range from 3,000 to 50,000, especially 20,000 to 30,000. the molecular weight is determined by the method described above but employing 1M NaOH as solvent and using the equation II above.

The styrene-maleic acid copolymers preferably have molecular weights of approximately 300,000. The molecular weight is determined by the same method but employing acetone as solvent and using the equation I above.

The most preferred copolymers are those of methyl and ethyl vinyl ether-maleic anhydride or acid described above.

Additional Components

It is to be understood that the compositions of the present invention may be supplemented by all manner of detergent components, either by including such components in the aqueous slurry to be dried or by admixing such components with the compositions of the invention following the drying step. Soil suspending agents at 0.1% to 10% by weight such as water-soluble salts of carboxymethylcellulose, carboxyhydroxymethylcellulose, and especially polyethylene glycols having a molecular weight of 400 to 10,000 are common components for the compositions of the present invention. Dyes, pigments, optical brighteners, and perfumes can be added in varying amounts as desired.

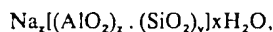
Other materials such as fluorescers, antiseptics, germicides, enzymes in minor amounts, anti-caking agents such as sodium sulfosuccinate, and sodium benzoate can also be added. Enzymes suitable for use herein include those discussed in U.S. Patents 3,519,570 and 3,553,139 to McCarty and McCarty *et al.*, issued July 7, 1970 and January 5, 1971, respectively.

Additional non-phosphorus containing alkaline detergency builder salts can also be added, although as stated earlier, high levels of highly alkaline builder salts should be avoided. In particular, the solution pH of the composition must be less than 11.5, the 'solution pH' being defined as the pH of a 0.5% solution in distilled water of the detergent composition.

Suitable examples of organic builders are the water-soluble salts of nitrilotriacetic acid, phytic acid, mellitic acid, benzene - 1,3,5 - tricarboxylic acid, citric acid, oxydisuccinic acid, carboxy - methyloxy succinic acid, 2 - oxa - 1,1,3 - propanetricarboxylic acid, cyclopentane - cis,cis,cis - tetracarboxylic acid, hexasodium - 1,3,3,4,5 - pentane hexacarboxylate, tetrasodium 1,1,3,3 - propane tetracarboxylate, hexapotassium cyclopentadienide pentacarboxylate, 2,3,4,5 - tetrahydrofuran - cis,cis,cis - tetracarboxylic acid and pyromellitic acid.

Inorganic builder salts include, for instance, alkali metal carbonates, tetraborates, pentaborates, aluminates, bicarbonates, sesquicarbonates, higher polyphosphates such as pentapolyphosphates and metaphosphates such as $\text{Na}_{16}\text{P}_4\text{O}_{43}$ and water insoluble zeolites or aluminosilicates. One such aluminosilicate which is useful in the compositions of the invention is an amorphous water-insoluble hydrated compound of the formula $\text{Na}_x(\text{xAlO}_2\text{ySiO}_2)_z$, wherein x is an integer of from 1 to 1.2 and y is 1, said amorphous material being further characterized by a Mg^{++} exchange capacity of from 50 mg eq., CaCO_3/g to 150 mg eq. CaCO_3/g . This ion exchange builder is more fully described in Ireland published patent application 1505/74, to B. H. Gedge et al filed July 16, 1974, herein incorporated by reference.

A second water-insoluble synthetic aluminosilicate ion exchange material useful herein has the formula



wherein z and y are integers of at least 6; the molar ratio of z to y is in the range from 1.0 to 0.5, and x is an integer from 15 to 264; said aluminosilicate ion exchange material having a particle size diameter from 0.1 micron to 100 microns; a calcium ion exchange capacity of at least 200 mg eq./g; and a calcium ion exchange rate of at least 2 grains/gallon/minute gram as described in Belgian Patent 814,874 herein incorporated by reference.

A further optional component of the present compositions is a suds depressant. Soap is an effective suds depressant, especially C_{16-22} soaps, for instance those derived by neutralisation of Hyfac (trade name) fatty acids. These are hardened marine fatty acids of chain length predominantly C_{18} to C_{20} . However, non-soap suds depressants are preferred. A preferred suds depressant comprises silicones. In particular, there may be employed a particulate suds depressant comprising silicone and silica releasably enclosed in a water soluble or water dispersable substantially non-surface active detergent-impermeable carrier. Suds depressing agents of this type are disclosed in British patent specification 1,407,997 incorporated herein by reference.

A very suitable granular (prilled) suds depressant product comprises 7% silica/silicone (85% by weight silanated silica, 15% silicone obtained from Messrs. Dow Corning), 65% sodium tripolyphosphate, 25% tallow alcohol (EO)₂₅ (i.e. condensed with 25 molar proportions of ethylene oxide), and 3% moisture. Also suitable and preferred is a combination of 0.02% to 5% by weight, especially about 0.3% of the composition, of a substantially water insoluble wax or mixture or waxes, melting at from 35°C to 125°C, and having saponification value less than 100, and a suds depressed amount, usually approximately 2% of the composition, of particulate suds depressant mentioned above. Suds depressant mixtures of this type are described in British patent specification No. 1,492,939 (application 10734/74), incorporated herein by reference.

A further desirable component of the detergent compositions of the present invention is an alkali metal silicate having the formula $n\text{SiO}_2\text{:M}_2\text{O}$ wherein n lies in the range from 0.5 to 4.0 and M is an alkali metal or mixtures thereof, such as the sodium or potassium salt, preferably sodium. This can be added in amounts generally up to 15% by weight. In those compositions comprising less than 25% phosphate builder, especially when the builder is based upon pyrophosphate or orthophosphate or mixtures thereof with tripolyphosphate, the molar ratio $\text{SiO}_2\text{:M}_2\text{O}$ is preferably greater than 1.5:1 and more preferably lies in the range from 2.4:1 to 4:1.

Preferred classes of silicate of this type are disclosed in Belgian patent Nos. 833,934 and 838,549 incorporated herein by reference.

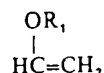
Another desirable component of the compositions of the invention is a bleaching agent, particularly a persalt bleaching agent selected from percarbonates, perborates, persulfates and perphosphates. This can be included in the compositions of the invention in an amount up to 40% by weight. However, it

is a feature of the invention that the compositions are effective in removing oxidizable type stains from fabrics washed therewith even in the absence of persalt bleaching agent, or in the presence of relatively low levels of persalt bleaching agent. Thus, preferred compositions contain no more than 3 to 20%, especially from 5 to 15% by weight of the persalt bleaching agent.

The compositions can also advantageously include a bleach activator which is normally an organic compound containing an N-acyl, or an O-acyl (preferably acetyl) group. Preferred materials are N,N,N',N'-tetraacetyl ethylene diamine and N,N,N',N'-tetraacetyl glycouril. The compositions can, in addition, advantageously include a cationic fabric softener or detergent.

Highly preferred compositions have a pH in 0.5% aqueous solution of less than 10.5, more preferably less than 10.0, and comprise

- (a) from 1 to 90%, more preferably from 5 to 40% of a synthetic organic detergent selected from anionic and nonionic detergents and mixtures thereof,
- (b) from 1 to 70%, more preferably from 5 to 50% of a phosphate builder which is a mixture of tripolyphosphate together with at least 2% of the phosphate builder of orthophosphate salts and/or at least 7% of the phosphate builder of pyrophosphate salts,
- (c) at least 0.2%, more preferably from 0.4 to 5% of a builder auxiliary comprising
 - (i) up to 4% by weight of a polyphosphonic acid selected from ethylene diamine tetra (methylene phosphonic acid) and diethylene triamine penta (methylene phosphonic acid) or a salt thereof,
 - (ii) up to 4% by weight of a copolymer of maleic acid or anhydride with a polymerisable unsaturated monomer having the formula:



wherein R₁ is a C₁ to C₁₂ alkyl group or a C₁ to C₁₂ acyl group, and is especially methyl or ethyl,

- (d) up to 15%, more preferably from 2 to 12%, of an alkali metal silicate having a molar ratio of SiO₂ to alkali metal oxide of from 0.5 to 4.0,
- (e) up to 2%, more preferably from 0.1 to 1.5% of a proteolytic enzyme, and
- (f) up to 40%, more preferably from 3 to 20%, of a persalt bleaching agent.

In preparing granular detergent compositions of the invention the components may be mixed together in any order and in powdery or in fluid form, e.g. in an aqueous dispersion. A preferred order of mixing components of a crutcher mix for a typical spray dried detergent composition of the invention would be:

Organic detergent paste usually containing organic surfactant, by-product (often sodium sulfate) and water;

The phosphate builder

Sodium silicate;

alkali (if required), e.g. sodium hydroxide sodium carbonate etc., especially alkali sufficient to neutralise polyacid sequestering agents.

Minor components;

Polyacid materials.

The composition can be sprayed dried or dried by other means, to provide a granular composition. Usually a moisture content of 3% to 10% is suitable to provide non-sticky free-flowing granules.

Liquid detergent compositions of the invention can contain, as optional ingredients, organic carriers or solvents such as lower aliphatic alcohols having from 2 to 6 carbon atoms and 1 to 3 hydroxyl groups; ethers of diethylene glycol and lower aliphatic mono-alcohols having from 1 to 4 carbon atoms; and mixtures thereof. Liquid compositions can also contain hydrotropes such as the water-soluble alkylaryl sulfonates having up to 3 carbon atoms in an alkyl group such as sodium, potassium, ammonium, and ethanol amine salts of xylene-, toluene-, ethylbenzene- and isopropylbenzene sulfonic acids.

EXAMPLES 1—7

Built low-sudsing detergent compositions were prepared having the formulae given below. To make each of the products, a slurry was prepared containing all the

components except where appropriate the perborate and enzyme and the slurry was then spray dried to form a granular intermediate. Sodium perborate was dry mixed with the intermediate granules to form the stated composition. All figures are given as % by weight.

5	EXAMPLE NO.	1	2	3	4	5	6	7	5
	Sodium linear dodecyl benzene sulphonate	8.0	7.0	1.0	8.1	—	—	8.0	
	dobanol 45-7 (9)	—	3.0	7.6	—	—	4.0	—	
10	Sodium tallow alcohol sulphate	—	2.5	—	1.9	10.0	1.0	—	10
	Sodium coconut soap	3.0	—	—	11.5	3.0	—	—	
	Sodium silicate (SiO ₂ : Na ₂ O 3.2:1)	6.1	10.1	10.1	10.1	10.1	6.0	10.0	
	Dobanol 45-4 (10)	—	—	4.0	—	2.0	8.0	—	
15	Sodium alkyl (C ₁₄ —C ₁₈) triethoxysulphate	—	5.5	—	—	—	2.0	4.0	15
	Sodium sulphate	25.3	29.3	13.5	10.5	21.0	34.8	18.9	
	Disodium orthophosphate	—	1.0	—	—	—	2.0	—	
	Tetra sodium pyrophosphate	36.0	17.0	19.0	23.0	28.0	32.0	16.0	
20	Sodium perborate, tetra hydrate	12.0	10.0	32.0	25.0	20.0	—	32.0	20
	Sodium carboxymethyl cellulose	0.8	0.8	0.8	0.8	0.8	0.8	0.8	
	Tallow Alcohol (EO) ₁₁	0.5	0.5	0.5	2.0	—	0.5	2.0	
25	Silicone prills (1)	2.0	2.0	—	2.0	2.0	2.0	2.0	25
	Microcrystalline wax (2)	0.3	0.3	0.5	0.3	0.3	0.3	0.3	
	Dequest 2060 (3)	—	—	1.5	1.0	—	—	—	
	Dequest 2040 (5)	1.0	—	—	0.5	—	1.0	1.0	
	Dequest 2010 (4)	—	1.0	—	—	1.0	—	—	
30	Empicryl (6)	—	—	—	1.0	—	—	1.0	30
	Gantrez AN119 (7)	1.0	—	1.0	—	1.0	—	—	
	Gantrez AN139 (8)	—	2.0	0.5	—	—	1.0	—	
	Proteolytic enzyme (11)	1.0	0.4	—	0.4	—	1.0	—	
	Water and miscellaneous	To 100%							
35	Notes:								35
	(1) comprising 0.14 parts by weight of an 85:15 by weight mixture of silanated silica and silicone, granulated with 1.3 parts of sodium tripolyphosphate, and 0.56 parts of tallow alcohol condensed with 25 molar proportions of ethylene oxide.								
40	(2) Witcodur 272 M.pt. 83°C. (Trade Name).								40
	(3) Trade name for diethylene triamine penta (methylene phosphonic acid), marketed by Monsanto.								
	(4) Trade name for ethane - 1 - hydroxy - 1,1 - diphosphonic acid, marketed by Monsanto.								
45	(5) Trade name for ethylenediamine tetra (methylene phosphonic acid), marketed by Monsanto.								45
	(6) Trade name; believed to be a copolymer of diisobutylene and maleic acid, MWt. about 5,000.								
50	(7) Trade name for maleic anhydride/vinyl methyl ether copolymer, believed to have an average molecular weight of about 240,000 marketed by GAF. This was prehydrolysed with NaOH before addition.								50
	(8) Trade name for maleic anhydride/vinyl methyl ether copolymer, believed to have an average molecular weight of about 500,000, marketed by GAF. This was prehydrolysed with NaOH before addition.								
55	(9) Trade name; primary C ₁₄₋₁₈ alcohols condensed with 7 molar proportions of ethylene oxide, marketed by Shell.								55
	(10) Trade name; primary C ₁₄₋₁₅ alcohols condensed with 4 molar proportions of ethylene oxide, marketed by Shell.								
	(11) Maxatase: 15% pure enzyme marketed by Gist-Brocades.								
60	These products provide good cleaning and whiteness maintenance characteristics and give little or no deposition of inorganic residues on washed fabrics or scaling of washing machine heaters.								60

Products with similar performance are obtained when the sodium alkyl benzene sulphonate is replaced by C₁₀₋₂₂ olefine sulphonates, C₁₀₋₂₀ paraffin sulphonates, and by zwitterionic detergents such as C₁₀₋₁₈ alkyl dimethyl ammonium propane sulphonate or hydroxypropane sulphonate.

Good performance is also obtained when Gantrez AN119 is replaced by, as their sodium salts, a copolymer of methyl methacrylate and maleic acid, the molar ratio of the monomers being about 1:1, of molecular weight about 10,000; an ethylene-maleic acid copolymer of molecular weight about 4,000, a propylene-maleic acid copolymer of molecular weight about 30,000; 1-hexene-maleic acid copolymer of molecular weight about 25,000; a vinyl pyrrolidone-maleic acid copolymer of molecular weight about 20,000; a 1:3 copolymer of acrylic acid and itaconic acid; a 1:4 copolymer of 3-butenic acid and methylenemalononic acid; a 1:9 copolymer of isocrotonic acid and citraconic acid; a 1:1.9 copolymer of methacrylic acid and aconitic acid; and a 1.2:1 copolymer of 4-pentenoic acid and itaconic acid.

EXAMPLES 8 to 12

Low sudsing detergent compositions have the following composition and are made by spray drying a slurry of the components, other than perborate and enzyme, in water.

Example No.	8	9	10	11	12
Sodium dodecylbenzene sulphonate	8.0	1.0	8.0	8.0	10.0
Dobanol 45-7 (1)	—	8.0	—	—	—
Sodium tallow alkyl sulphate	12.0	—	—	2.0	—
Dobanol 45-4 (1)	—	4.0	—	—	—
Acidified Sodium silicate (SiO ₂ :Na ₂ O 3.3:1) (3)	6.0	6.0	7.0	6.0	10.0
Sodium sulphate	43.2	19.8	38.8	26.6	17.0
Sodium tripolyphosphate	6.0	—	6.0	2.0	2.0
disodium pyrophosphate	8.0	38.0	10.0	14.0	14.0
sodium carboxymethyl cellulose	1.0	1.0	0.5	0.5	—
Magnesium silicate	—	2.0	—	—	—
Silicone prills (1)	2.0	—	2.0	1.5	—
Microcrystalline wax (1)	0.3	—	0.3	0.5	—
Sodium perborate	—	—	20.0	10.0	32.0
Hyfac (2)	—	—	—	—	3.0
Tallow alcohol EO ₁₁	—	—	0.5	1.0	2.0
Gantrez AN119 (hydrolysed) (1)	1.5	1.0	—	1.0	1.5
Dequest 2060 (1)	1.0	—	1.0	—	0.5
Dequest 2040 (1)	—	0.5	—	0.5	—
Proteolytic enzyme (1)	—	0.4	0.4	1.0	—
Sodium pentapolyphosphate	—	—	2.5	2.0	—
Optical brightener (stilbene type)	—	0.2	0.2	—	—
Moisture and miscellaneous	To 100%				

These compositions provide good cleaning and whiteness maintenance, with very low deposition of inorganic matter on fabrics or washing machine heaters.

Notes:

(1) As in Examples 1—7.

(2) Trade name: C₁₈₋₂₀ saturated fatty acids.

(3) Acidified sodium silicate prepared by adding 20.6 grams of unhardened tallow fatty acid having a molecular weight of about 275 to 10,882 grams of liquid silicate having an SiO₂:Na₂O ratio of 3.2:1 and containing 40% solids; heating the silicate to 150°F and agitating the silicate premix for 5 minutes, before adding to the crutcher.

		EXAMPLES 13-17					
		13	14	15	16	17	
5	Example No.						
	Sodium linear C ₁₂ alkyl benzene sulfonate	8.0	1.0	8.0	8.0	8.0	
	Sodium coconut soap	12.0	—	3.0	—	—	5
	Sodium silicate (SiO ₂ /Na ₂ O=2.0)	6.1	6.1	6.1	6.1	6.1	
	Dobanol 45-7 (1)	—	7.0	2.0	—	—	
10	Sodium orthophosphate Na ₂ HPO ₄	11.6	8.0	9.2	12.8	12.2	10
	Dobanol 45-4 (1)	—	4.0	—	—	—	
	Sodium tripolyphosphate	1.5	7.9	7.9	1.5	—	
	Sodium pentapolyphosphate	3.0	—	3.0	3.0	3.0	
	Dequest 2040 (1)	1.0	2.0	—	0.5	2.0	
15	Dequest 2060 (1)	—	—	0.5	—	—	15
	Gantrez AN119 (1)	1.0	2.0	1.0	0.5	0.5	
	Ethylene diamine tetra-acetic acid	0.2	0.2	0.2	0.2	0.2	
	Silicone prills (1)	2.0	—	2.0	2.0	2.0	
	Proteolytic enzyme (1)	0.3	0.3	0.3	0.3	0.3	20
20	Microcrystalline wax (1)	0.3	—	0.3	0.3	0.3	
	Sodium perborate	—	32.0	12.0	20.0	32.0	
	Tallow alcohol	0.5	—	0.5	0.5	0.5	
	Tallow alcohol (EO) ₁₁	10.0	18.0	32.0	32.0	21.0	25
	Sodium sulfate	—	—	—	—	—	
Moisture & Miscellaneous		to 100%					

(1) See Examples 1 to 7.

These products provide good cleaning and whiteness maintenance characteristics and give little or no deposition of inorganic residues on washed fabrics or scaling of washing machine heaters.

		EXAMPLES 18-23						
		18	19	20	21	22	23	
35	Sodium linear dodecyl benzene sulphonate	8.0	8.0	5.0	8.0	1.0	7.0	
	Sodium tallow alkyl sulphate	1.0	12.0	—	—	—	—	35
	Sodium silicate (SiO ₂ /Na ₂ O=2:1)	6.1	6.1	—	6.1	—	6.1	
	Sodium silicate (SiO ₂ /Na ₂ O=1.6:1)	—	—	6.1	—	6.1	—	40
	Dobanol 45-7 (1)	—	—	3.0	3.0	8.0	4.0	
40	Sodium sulphate	24.7	23.0	24.2	33.7	6.0	20.6	
	Dobanol 45-4 (1)	—	—	—	—	4.0	—	
	Disodium orthophosphate	7.5	25.0	1.0	4.8	1.0	1.0	
	Sodium coconut soap	—	—	—	—	12.0	—	45
	Tetrasodium pyrophosphate	7.1	5.0	7.0	2.4	7.0	4.0	
45	Magnesium silicate (SiO ₂ /MgO ratio 1:1)	—	2.0	—	—	—	—	
	Pentasodium tripolyphosphate	—	—	25.0	8.8	28.0	13.0	
	Sodium pentapolyphosphate	2.0	—	—	2.0	—	2.0	50
	Sodium perborate tetrahydrate	32.0	—	10.0	20.0	15.0	30.0	
	Sodium carboxymethyl cellulose	0.8	1.0	0.8	0.8	0.8	0.8	
55	Polyhydroxy acrylate (3)	—	1.0	—	—	—	—	55
	Silicone prills (1)	2.0	—	2.0	2.0	—	2.0	
	EDTA	—	0.2	—	0.2	—	0.2	
	Hyfac (2)	—	3.0	—	—	—	—	
	Tallow alcohol (EO) ₁₁	0.5	2.0	—	0.5	—	0.5	
60	Gantrez AN139 (1)	—	3.0	—	—	0.5	—	60
	Microcrystalline wax (1)	0.3	—	0.3	0.3	—	—	
	Gantrez AN119 (1)	1.2	1.0	0.5	1.0	0.5	1.0	

EXAMPLES 18—23 (contd.)

		18	19	20	21	22	23	
	Dequest 2040	(1)	—	1.0	0.5	1.5	1.0	1.0
	Dequest 2060	(1)	0.1	—	—	—	—	—
5	Enzyme	(1)	0.3	—	1.0	—	0.4	—
	Water & Miscellaneous		To 100%					5

(1) See Examples 1 to 7.

(2) See Examples 8 to 12.

10 (3) Obtained from Messrs. Solvay and Cie S.A., molecular weight believed to be about 50,000. 10

N.B.

15 Examples 20, 22 and 23 are prepared by spray-drying detergent compositions built with "pure" sodium tripolyphosphate. The indicated values of orthophosphate and pyrophosphate include *all* salts thereof resulting from the hydrolytic degradation of the tripolyphosphate during spray drying. 15

The above products provide good cleaning and whiteness maintenance characteristics and give little or no deposition of inorganic residues on washed fabrics or scaling of washing machine heaters.

20 Good performance is also obtained when Gantrez AN119 is replaced by, as their sodium salts, a copolymer of methyl methacrylate and maleic acid, the molar ratio of the monomers being about 1:1, of molecular weight about 10,000; an ethylene-maleic acid copolymer of molecular weight about 4,000; a propylene-maleic acid copolymer of molecular weight about 30,000; 1-hexene-maleic acid copolymer of molecular weight about 25,000; a vinyl pyrrolidone-maleic acid copolymer of molecular weight about 26,000; a styrene-maleic acid copolymer of molecular weight about 20,000; a 1:3 copolymer of acrylic acid and itaconic acid; a 1:4 copolymer of 3-butenic acid and methylenemalononic acid; a 1:9 copolymer of isocrotonic acid and citraconic acid; a 1:1.9 copolymer of methacrylic acid and aconitic acid; and a 1.2:1 copolymer of 5-pentenoic acid and itaconic acid. 25

EXAMPLES 24—26

Heavy duty liquid detergent compositions comprise:

		24	25	26	
	Triethanol ammonium dodecyl benzene sulphonate	20	20	15	
	Dobanol 45-7	—	20	10	
35	Dipotassium orthophosphate	10	—	1	35
	Tetrapotassium pyrophosphate	6	14	7	
	Pentapotassium tripolyphosphate	—	—	30	
	Sodium silicate (SiO ₂ :Na ₂ O=3.2:1)	—	5	—	
	Gantrez AN139	1	1	0.5	
40	Dequest 2040	1	1	0.5	40
	sodium toluene sulphonate	6	6	10	
	Ethanol	—	10	5	
	Water and miscellaneous	56	24	21	

45 The above compositions provide good cleaning and whiteness maintenance with very low deposition of inorganic residue on fabrics or washing machine surfaces. 45

WHAT WE CLAIM IS:—

1. A built detergent compositions having a pH of 0.5% aqueous solution of less than 11.5, the composition comprising
- 50 (a) from 1 to 90% of an organic detergent selected from anionic, nonionic, amphoteric, and zwitterionic detergents and mixtures thereof, 50
- (b) from 1 to 70% of a phosphate builder selected from orthophosphate, pyrophosphate and tripolyphosphate salts, and mixtures thereof, and
- 55 (c) at least 0.2% of a builder auxiliary comprising a mixture of: 55
- (i) up to 4% by weight of a polyphosphonic acid or salt thereof, and
- (ii) up to 4% by weight of a homo- or co-polymeric polycarboxylic acid or salt thereof, said polycarboxylic acid having a formula comprising at least two carboxyl radicals separated from each other by not more than two carbon atoms.

2. A composition according to Claim 1 containing from 5 to 50% of phosphate builder salt.

3. A composition according to Claim 1 containing phosphorus in an amount not exceeding that equivalent to 45% sodium tripolyphosphate.

5 4. A composition according to any of Claims 1 to 3 in which at least 2% by weight of the phosphate builder is a water-soluble inorganic orthophosphate salt. 5

5. A composition according to Claim 4 containing from 2 to 30% of the orthophosphate salt.

10 6. A composition according to any preceding Claim in which at least 7% by weight of the phosphate builder salt is a water-soluble inorganic pyrophosphate salt. 10

7. A composition according to Claim 6 containing from 2 to 35% of the pyrophosphate salt.

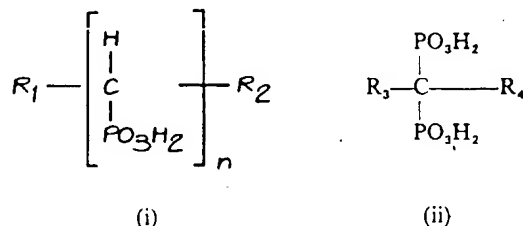
15 8. A composition according to any preceding Claim comprising pyrophosphate and tripolyphosphate salts in a weight ratio in the range from 5:1 to 1:4. 15

9. A composition according to any of Claims 1 to 7 in which the weight ratio of orthophosphate to pyrophosphate salts is in the range from 9:1 to 3:7.

10. A composition according to any preceding Claim containing from 0.4 to 5% of the builder auxiliary.

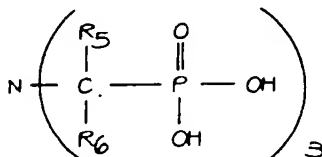
20 11. A composition according to any preceding Claim containing from 0.5 to 3.5% of each component of the builder auxiliary. 20

12. A composition according to any preceding Claim wherein the polyphosphonate is an acid or salt thereof of formula



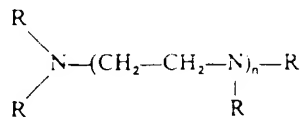
25 wherein R_1 and R_2 are hydrogen or CH_2OH ; n is an integer of from 3 to 10; R_3 is 25
hydrogen, alkyl containing from 1 to about 20 carbon atoms, alkenyl containing
from 2 to about 20 carbon atoms, aryl, phenylethenyl, benzyl, halogen, amino,
substituted amino, $-CH_2COOH$, $-CH_2PO_3H_2$, $-CH(PO_3H_2)(OH)$ or
30 $-CH_2CH(PO_3H_2)_2$; and R_4 is hydrogen, lower alkyl, halogen, hydroxyl, 30
 $-CH_2COOH$, $-CH_2PO_3H_2$, or $-CH_2CH_2PO_3H_2$.

13. A composition according to any of Claims 1 to 11 wherein the polyphosphonate is an acid or salt thereof of formula



wherein R_5 and R_6 represent hydrogen or C_1-C_4 alkyl radicals.

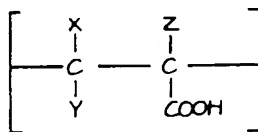
35 14. A composition according to any of Claims 1 to 11 in which the 35
polyphosphonate has the general formula



40 wherein n is an integral number from 1 to 14, and each R is individually hydrogen 40
or $CH_2PO_3H_2$ or a water-soluble salt thereof, provided that at least half of the
radicals represented by R are $CH_2PO_3H_2$ radicals or water-soluble salts thereof.

15. A composition according to Claim 14 in which the polyphosphonate is ethylene diamine tetra (methylene phosphonic acid) or diethylenetriamine penta (methylene phosphonic acid) or salts thereof.

16. A composition according to any preceding Claim in which the polycarboxylic acid has the general formula:

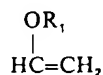


wherein X, Y, and Z are each selected from the group consisting of hydrogen, methyl, aryl, alkaryl, carboxyl, hydroxyl and carboxymethyl; at least one of X, Y, and Z being selected from the group consisting of carboxyl and carboxymethyl, provided that X and Y can be carboxymethyl only when Z is selected from carboxyl and carboxymethyl and wherein only one of X, Y, and Z can be methyl, aryl, hydroxyl and alkaryl.

17. A composition according to Claim 16 in which the polymeric polycarboxylic acid is derived from maleic acid or maleic anhydride monomer.

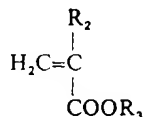
18. A composition according to any preceding Claim in which the polymeric polycarboxylic acid has an average molecular weight in the range from 500 to 2,000,000 and which is a copolymer of a polycarboxylic acid monomer and a polymerizable unsaturated monomer selected from

(a)



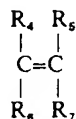
wherein R₁ is a C₁ to C₁₂ alkyl group or a C₁ to C₁₂ acyl group, R₁ optionally being hydroxy substituted,

(b)



wherein R₂ is H or CH₃ and R₃ is H, or a C₁ to C₁₀ alkyl group, R₂, R₃ optionally being hydroxy substituted,

(c)



wherein each of R₄ to R₇ is H or an alkyl group such that R₄ to R₇ together have from 1 to 20 carbon atoms, R₄—R₇ each optionally being hydroxy substituted,

(d) N-vinyl pyrrolidone,

(e) Styrene.

19. A composition according to Claim 18 in which the polymeric polycarboxylic acid is a copolymer of maleic acid or maleic anhydride with methyl vinyl ether or ethyl vinyl ether.

20. A composition according to any preceding Claim comprising from 5 to 40% of organic detergent.

21. A composition according to any preceding Claim comprising from 1 to 12% of alkali metal silicate having a molar ratio of SiO₂ to alkali metal oxide of from 0.5 to 4.0.

22. A composition according to any preceding Claim comprising from 0.1 to 1.5% of proteolytic enzyme.

23. A composition according to any preceding Claim comprising from 3 to 20% by weight of a peroxy salt bleaching agent.

24. A composition according to Claim 1 substantially as hereinbefore described with reference to any one of the Examples.

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